Chapter 4
Process Intensification of Biofuel Production from Microalgae

Saurabh Joshi and Parag Gogate

Abstract A tremendous increase in population has also led to a significant increase in the demand for energy leading to search for alternatives which can match up with the current requirement quantitatively and also qualitatively as a green energy carrier. Fuels derived from algal biomass can be one of the potential alternatives, as microalgae possess higher nutrients, required lipids and CO_2 uptake capacity and can be grown quickly on nonarable land throughout the year without their interference in food supply chain. The quantum of biodiesel produced from microalgae can be about 10–20 times higher than that obtained from terrestrial plants. Microalgae also help in reducing global warming by capturing CO_2. The cost of production of biofuels from microalgae is the current setback which can be overcome by taking into consideration a biorefinery approach which can give multiple products with same expenditure as well as using some process intensification approaches. Process intensification plays a major role in reducing the cost and also can lead to use of less quantum of materials and lower operating temperatures. The present chapter will focus on analyzing the process intensification aspects applied to biofuels production from microalgae. The initial sections will cover the details of the types of microalgae and their harvesting techniques, followed by the discussion on the different approaches used to extract bio-oil from microalgae, and then the production of different biofuels. Intensification can be applied to both the extraction and the actual reaction for production of biofuels. The chapter will also focus on the mechanism of intensification using different approaches such as ultrasound, microwave, ultraviolet, and oscillatory baffled reactors. An overview of the literature will be presented so as to give guidelines about the possible reactor designs and operating parameters also highlighting the process intensification benefits that can be obtained. Overall, the work is expected to bring out critical analysis of the different approaches and the expected benefits due to the use of process intensification also enabling understanding of the reactor designs and operating parameters.

S. Joshi · P. Gogate (✉)
Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai 40019, India
e-mail: pr.gogate@ictmumbai.edu.in

E. Jacob-Lopes et al. (eds.), *Energy from Microalgae*, Green Energy and Technology, https://doi.org/10.1007/978-3-319-69093-3_4

Keywords Microalgae · Process intensification · Biofuels · Biorefinery
Reactor designs

1 Introduction

1.1 Need of Biofuels

Greenhouse gases (GHG) are mainly produced by the transportation and energy-producing sectors. Along with GHG, other pollutants like SO_x, NO_x, CO, volatile compounds, and particulate matter are also released into the atmosphere. Day by day, the global energy consumption is increasing, also resulting in an increase in pollution which further raises the concern of global warming. To cope up with the energy requirements and at the same time reduce the pollution, development of sustainable alternative energy sources has become the major goal. Many countries are working on utilizing different alternatives like solar energy, geothermal, wind, hydroelectric, thermal or photovoltaic, and biofuels. Every alternative generally comes with its own pros and cons, and the development of optimum and feasible alternative with time is the desired solution. Among the biofuels, Second-generation biofuels (biodiesel, bioethanol, and biogas) offer important alternatives and can be produced from sustainable resources available, with lesser or practically no emissions on their combustion. Biodiesel can be produced from non-edible oils, waste cooking oil, waste grease, or animal fats, whereas bioethanol and biogas can be produced from agricultural waste (wheat straw, corn cobs, etc.) and other sustainable materials. The availability of these materials, expensive processing, and production cost cannot fulfill the current supply and demand of energy requirements in a most efficient manner. Biofuel production from microalgae which comes under third-generation biofuels has now become a significant research area. Advantages like easy cultivation, non-competitiveness with food supply chain, higher lipid content, and less processing are obtained based on the use of microalgae which help in overall reduction of biofuel production cost.

1.2 Microalgae

Microalgae are unicellular microscopic organisms found in both marine and freshwater environment. They perform photosynthesis with efficiency higher than that of crops and consist of various components which can be utilized for many commercial purposes such as in the food, cosmetic, and high-value specialty molecules industry. Capability to naturally produce many unusual and different fats, bioactive compounds, sugars, etc., comes from their diversified genetic group which also comes with different physiological and biological characteristics. Microalgae mainly consist of proteins, carbohydrates, fats, and nucleic acids which

directs the utilization of microalgae in different ways (Fig. 1). These components vary according to the species observed in different areas depending on the surrounding conditions like temperature, nutrients, pH, and light intensity.

Microalgae production offers advantages like high rates of production, and less doubling time as compared to plants and other biomass feedstocks and can help in utilizing the non-arable land with possible cultivation using the saline or waste water. It has the ability to sustain in environments having nutrient limitations and varying pH. Actually, under specific stress conditions, it produces high levels of lipids which can be further converted to biofuels efficiently. Currently, the cost of cultivating and harvesting microalgae is a setback which requires a greater investment as compared to other options available. Study on microalgae production approaches is required on higher scale as they may consist of untapped information which can be utilized for further good of mankind, though this is not the focus of the current chapter.

Depending on the metabolism, microalgae can be classified into four groups, that is, photoautotrophic, heterotrophic, photoheterotrophic, and mixotrophic. Microalgae can also be differentiated based on the source of cultivation such as freshwater or marine water. Freshwater algae are found to be grown on rocks under water and in mud of streams and river but the growth observed is more in still water than in flowing water. *Chlorophyta* (green algae), *Rhodophyta* (red algae), and *Bacillariophyta* (diatoms) are the examples of freshwater algae. The main problem is, however, the contamination of freshwater caused due to algae growth. Marine algae cultivation can help in boosting the economics involved in biomass

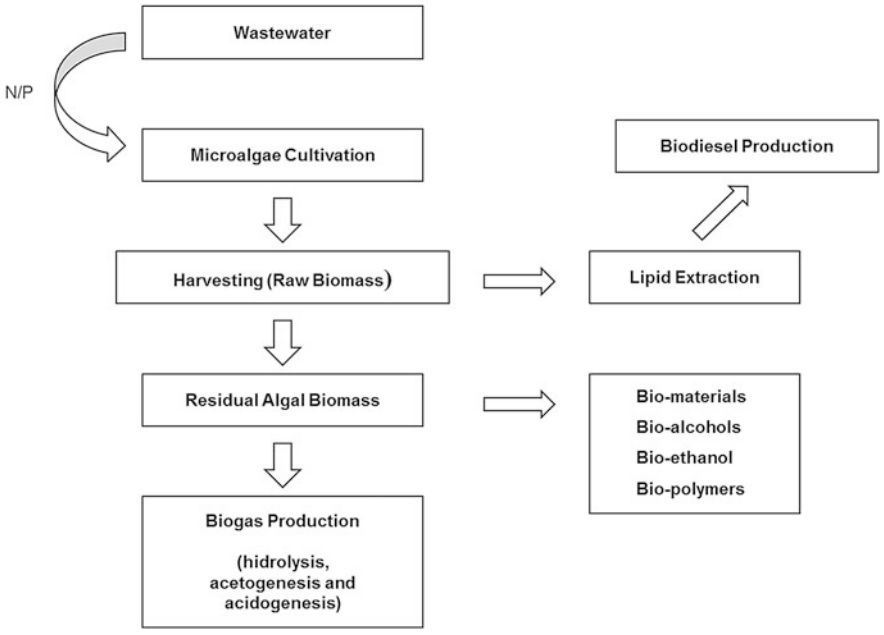

Fig. 1 Biofuels and other products which can be obtained by processing of microalgae

cultivation as they can be grown in brackish water, near coastal areas, floating on sea water, or in salt marshes. This also comes with some problems like effects on natural marine flora; premature rupture of microalgae cells due to high salinity of water and requirement of pretreatment of marine water, which adversely affects the economic feasibility. Overall, there is a need of deeper insight on the cultivation source and production approaches to be used for microalgae including the possible use of wastewater for microalgae cultivation which leads to solving of both the issues, that is, treatment of wastewater and cultivation source.

1.2.1 Lipid Content in Microalgae

Higher level of lipid content is an important parameter for utilization of microalgae. Few microalgae like *Botryococcus braunii* and *Chlorella emersonii* are naturally capable to produce up to 75% of lipid content (g lipids/dry weight). *Chlorella vulgaris and Dunaliella* sp. can reach up to 50% productivity under normal conditions. Lipid content in most of the microalgae species is generally between 20 and 50%. Profile of fatty acids also has a positive impact on biodiesel production (Priyadarshani and Rath 2012). Lipid profile is typically species-specific. Process improvement approaches can be efficiently applied to maintain desired specific conditions for microalgal growth (Patel et al. 2016). Growth parameters like nutrient availability, environmental factors, and cultivation type have a significant effect on microalgae lipid content. It has been reported that lipid production can be induced by nutrient-specific stress, for example, nitrogen starvation causes higher lipid production (Rodolfi et al. 2009). Similarly, phosphate content also has an effect on lipid productivity though it gives stronger increase in biomass content instead of lipid content (Xin et al. 2010). Salt stress can also have an impact on the production of lipids in microalgae as reported by Takagi et al. (2006). The microalgae grown in water with higher concentration of salts, that is, >1 M NaCl concentration were reported to have high lipid productivity as compared to those grown in 0.5 M NaCl solution. To get higher content of lipid is the main target which can be achieved with help of process optimization of required parameters. In the above cases, process improvement approaches can be helpful in identifying the desired conditions for microalgae growth and can increase the overall yield of lipids. The application of ultrasound as a process intensification approach can also enhance the growth of microalgae and increase the lipid production. In the study carried out by Han et al. (2016), it was reported that exposing the microalgae to different powers of ultrasound increased the overall yield and lipid content by 1.86 and 1.46 times, respectively.

2 Cultivation of Microalgae

Microalgae are cultivated using two main approaches based on the open pond system (raceway ponds, natural ponds, circular ponds, and inclined systems) and closed system (PBR-photobioreactor). Since 1950s, the open pond system has been

used to cultivate the microalgae with the usage of natural water bodies like lakes, ponds or lagoons, and artificial water supply systems. Use of closed system prevents the contamination by other microbial species. Currently, many designs have been used for closed systems based on PBR such as flat plate, column or tubular and are classified on the basis of mode of operation and shape. Tubular and flat plate PBR are the most commonly used closed system PBR. The closed system comes with advantages but requires further detailed study on scale up, parameter control and cost, and currently, it is not considered economically feasible at large scale.

Process intensification can be applied to PBR considering aspects like carbon supply decoupling and mixing which will help significantly in ensuring proper supply of carbon dioxide and removal of oxygen. It has been reported that using a hollow fiber membrane can solve the problem of inefficient transfer up to an extent (Carvalho et al. 2006). Obtaining the desired increase in internal surface area and application of data on measurement, modeling, and control can also be a good process improvement approach. In one of the studies, concentrated microalgae cultivation in continuous mode was performed using resonant ultrasound field (RUF) which helped to enhance medium replacement process also resulting into process intensification benefits. The optimized process parameters reported were 1 MHz frequency and output intensity of 8 W/cm^2 with a circulating velocity of 2 mL/min leading to 93% collection of microalgae in 2 h (Lee and Li 2016). Pfaffinger et al. (2016) investigated the use of flat plate gas lift photobioreactor with continuous illumination using LEDs. The study showed an increase in algal productivity by 113% and lipid productivity by 59%. The design of the oscillatory baffled reactor was also utilized in developing the PBR which gave increased gas transfer and reported to improve overall economics of microalgae production (Abbott et al. 2015).

Other reactor configurations which have been also studied are rotating disk biofilm reactor and biofilm reactor which were reported to give a yield of 3.2 and 3.64 g/m ^{2}/day, respectively, and also reported to help in overcoming the issues of suspended cultures (Sebestyen et al. 2016; Choudhary et al. 2017).

2.1 Cultivation of Microalgae from Wastewater

High content of nitrogen and phosphorous in wastewater makes it one of the best cultivation systems for microalgae. Total organic carbon of the wastewater can be utilized by some of the microalgal species as food source (Wang et al. 2010). Considering higher costs involved in microalgae production and wastewater treatment, it can be a boon if microalgae can be produced using wastewater as the cultivation medium. Algal ponds can be used for cultivation of microalgae using the municipal, industrial, and agricultural wastewaters. Secondary-treated wastewater contains nitrogen and phosphates in the range of 20–40 and 1–10 mg/L, respectively, which can help most microalgae strains to achieve high productivities (Olguín 2012). Microalgae release oxygen which in turn can be used by other microorganisms increasing the overall efficiency of aerobic degradation that can

further decrease the BOD and COD of the wastewater, achieving the desired objective of wastewater treatment as well.

Several studies have been reported for reduction in nitrogen and phosphorous containing compounds coupled with biomass growth. Removal of nitrogen and phosphorus was reported using *C. vulgaris* with a removal efficiency of 72 and 28%, respectively (Aslan and Kapdan 2006). *Chlamydomonas polypyrenoideum* was used in a study of dairy wastewater treatment, and it was reported that nitrate level could be reduced by 90%, ammonia by 90%, phosphorus by 70%, and COD by 60% in 10 days (Lu et al. 2015). *Chlorella sorokiniana* when used for treatment of alcohol distillery wastewater in a 50 L PBR could decrease the nitrate content by 95%, phosphate by 77%, and sulfate by 35% in a time period of 3 days (Solovchenko et al. 2014). In a study performed by Li et al. (2011a), it has been reported that using bench scale continuous cultures, 0.92 g/L/d productivity of Chlorella strain was achieved using wastewater rich in ammonium, phosphorus, and organic matter with a COD of 1300 mg/L. Emerging contaminants (EC) can also be treated by microalgae to some extent as compared to other commonly available biological treatment. Microalgae can treat emerging contaminants in sequence of pharmaceuticals > PCPs (personal care products) > EDCs (endocrine disruption chemicals) > pesticides (Ahmed et al. 2017). Microalgae can also be used in the removal of heavy metals and can be employed based on the detoxification and biosorption techniques (Suresh Kumar et al. 2015). It can be clearly concluded from the studies mentioned above that cultivation of microalgae from wastewater not only reduces the pollution caused but also provides a rich sustainable feedstock in the form of algal growth which can be further utilized in biofuel production.

3 Harvesting

Process of harvesting consists of separation of biomass from the medium used for cultivation of microalgae. It is basically a separation process which separates microalgae biomass from cultivation medium. It is important that the process is a cost-effective one as it makes to about 20–30% of the total cost required for the whole process. Filtration, centrifugation, flocculation and floatation, gravity sedimentation, etc., are the techniques mostly used for this operation. The exact method is selected based on the cell size, cell density, and total quantity of the product to be separated. New techniques of harvesting and application of process intensification have also been reported based on techniques like flocculation assisted by the use of magnetic microparticles (Vergini et al. 2016), magnetic membrane filtration (Bilad et al. 2013), sedimentation assisted by the use of polymers (Zheng et al. 2015), electrical methods like electro-coagulation-filtration (ECF) (Gao et al. 2010) and electrochemical harvesting (ECH) (Misra et al. 2015). Low-frequency ultrasound can also be applied to the grown microalgal cells which results in decrease in the buoyancy and increases the sedimentation of the cells resulting in 90–92% as the harvesting efficiency (Kim et al. 2013).

4 Recovery of lipids and other products

Generally, the process of drying followed by disruption and solvent extraction is used for the recovery of desired products including the lipids from microalgae. Drying can be performed based on sun drying, spray drying, drum drying, and freeze drying. Sun drying is the most affordable option and can be employed effectively in biofuels production while spray drying hampers the overall economics of process when used for biofuels or protein production. Drum drying and freeze drying are also not the most viable options considering the application of biofuel production. After drying process, the dried biomass is subjected to disruption depending on the nature of desired product to be recovered or cell wall strength of microalgae, which affects the recovery. Disruption is carried out by mechanical processes (bead mills, autoclave, cell homogenizer, spray drying, ultrasound, etc.) and non-mechanical processes (using organic solvents, freezing, acid and osmotic shock, alkali, and enzyme treatment).

Microwave and ultrasound are emerging potential technologies which can be employed in the cell disruption process, also giving process intensification benefits. Application of Process intensification approaches helps this process to be performed with the achievement of economic feasibility. It has been reported that microwave and ultrasound are the technologies which result in higher amount of disruption as compared to other available technologies (Prabakaran and Ravindran 2011). Table 1 illustrates a few examples in which the ultrasound has been employed as a effective process for disruption of biomass.

Table 1 Ultrasound use for disruption of microalgae

Specie	Biomass concentration (g/L)	Frequency (kHz)	Time (min)	Yield of lipid	Reference
Chlorella sp.	5	50	15	156.6 mg/L	Prabakaran and Ravindran (2011)
C. vulgaris	5	10	5	6.1–8.8 mg/L	Lee et al. (2010)
C. vulgaris	2.5	–	17.5	2.9 times increase in lipid content	Zheng et al. (2011)
N. oculata	5	20	30	Increase in oil recovery to 0.24% from 0.15%	Adam et al. (2012)

Solvents such as ethanol, hexane, or a mixture of hexane-ethanol are generally used for extraction of lipids to be used in biodiesel production. Sometimes methanol can be also used which can serve both the purpose of extraction and as a reactant in the subsequent transesterification reaction. The extraction process is limited by mass transfer and hence the use of process intensification approaches can be very beneficial. Patil et al. (2011a, b) performed microwave-assisted direct transesterification of the microalgae using methanol and reported yield of up to 77% with process optimization. Wahlen et al. (2011) studied the comparison of the use of wet and dry algae biomass in direct transesterification and also the effect of water content on FAME yield. It was reported that 30 mg FAME can be produced from 100 mg of wet algae sample via this process of direct transesterification as compared to the conventional process which gave only 27 mg FAME from 100 mg. Study also concluded that the wet biomass of algae can be effectively utilized for biodiesel production based on nullifying the effects of water content by the addition of higher amount of methanol, also giving advantages of elimination of processing step.

Super critical extraction is also one of the techniques efficiently used for intensified extraction of lipids from microalgae. Many process intensification benefits have been reported with the use of super critical conditions as mentioned in Table 2. Similarly, ultrasound has also been applied in few studies to give intensified extraction. Ferreira et al. (2016) performed a study using low-frequency ultrasound with pure solvent (n-hexane and ethanol) and binary mixture of solvents (chloroform:ethanol; chloroform:isopropanol; chloroform:methanol; n-hexane: methanol; nhexane: isopropanol; n-hexane:ethanol, and n-hexane:2-butanol). It was reported that the frequency of 50/60 kHz with binary solvent of nhexane: isopropanol in 2:1 ratio was the most effective. It was also reported that the energy requirements were lesser as compared to conventional Soxhlet extraction and super critical extraction (SRE).

Table 2 Different super critical extraction (SRE) processes for microalgae processing with process parameters and yields (Lee et al. 2014)

Specie	Solvent/co-solvent	Temperature (°C)/ pressure (MPa)	Time (min)	Yield (%)
Chlorella vulgaris	Ethanol (6.6 ethanol/solids mass ratio) H_2O (10.1 wt%)	325	120	100
Chlorella vulgaris	Methanol (4 mL/g) H_2O (80 wt%)	175/2.2	240	89.7
Nannochloropsis (CCMP1776)	Methanol (9.0 mL/g) H_2O (ratio not mentioned)	255/8.27	25	84.1
Nannochloropsis salina	Ethanol (9 mL/g) H_2O (60 wt%)	265/8.27–9.30	20	67
Nannochloropsis salina	Ethanol (9 mL/g) H_2O (ratio not mentioned)	260/8.0	25	30.9
Chlorella protothecoids	Ethanol (20:1 ethanol/fatty acid molar ratio)	275/20.0	180	89

5 Process Intensification Strategies for Biofuel Production from Microalgae

Depletion of current fossil fuel reserves and pollution due to emissions from the usage of these fossil fuels have created a situation where there is a need to focus on fuels which can be produced in an easy manner and cause lesser emissions on use. Biofuels like biodiesel, bioethanol, and biogas are the alternatives which can replace the conventional fossil fuels. These biofuels can be produced from microalgae which are a rich source of biomass and can be utilized in a sustainable manner as it can be grown without the competition to food chain and has the energy content higher than that of the other biomass sources available. Biodiesel is produced via transesterification reaction of oil with a methanol to yield fatty acid methyl esters (FAME). Bioethanol is mostly produced by anaerobic fermentation of sources which are rich in sugars and starch using yeast as the microbial culture. Biogas is also obtained via anaerobic fermentation based on the use of methanogenic culture to utilize the biodegradable content available in feedstock. Due to high lipid content, microalgae can be effectively utilized for biodiesel production though their ability to accumulate starch and cellulose also make them suitable to be used for bioethanol and biogas production (Gendy and El-Temtamy 2013). Biodiesel is indeed the most common biofuel produced from microalgae as observed in open literature though some work has also been carried out to produce bioethanol and biogas from microalgae.

5.1 Biodiesel

Biodiesel is mostly produced from virgin vegetable oils, waste cooking oil, animal fats, and non-edible oils. The main advantage of biodiesel is that the physical properties are same as that of diesel obtained from crude oil, and hence, it can be used directly in diesel engine. The raw material which is selected for the production contributes a major proportion in the overall production cost as it depends on different factors like ease of availability, actual cost, and characteristics of oil. Thus, selection of the material plays a major role in process economics. The reaction involved in biodiesel production is the reaction of oil (triglycerides) with methanol in the presence of catalyst, and the product produced is fatty acid methyl ester (FAME) which is commonly called as the biodiesel.

Biodiesel can be produced by catalytic, non-catalytic, and in situ transesterification reactions. Catalytic process involves the use of homogenous, heterogeneous, and enzymatic catalyst. Non-catalytic process involves the use of methanol at critical temperature with possible simultaneous extraction and transesterification process. In situ transesterification is a process similar to the non-catalytic process performed at higher temperature and pressure and offers advantages as minimal usage of solvents, easy separation of products, and lesser reaction time. We now present an overview of important production approaches as catalytic (both homogeneous and heterogeneous) and in-situ transesterification.

5.1.1 Catalytic Homogenous Transesterification

Base Catalyst

In transesterification reaction, base catalysts are mostly used as they are cheaply available and allow the usage of moderate reaction temperature and pressure which helps in carrying out the process with favorable conditions. Base catalysts also give higher yield in shorter period of time as compared to other catalysts (Schuchardt et al. 1998). Bases such as KOH, CH_3ONa, NaOH, and others are reported to catalyze the reaction via deprotonating the alcohol to produce active RO^- species which further react with the carbonyl group and get converted into final transesterified product ($RCOOR^I$). The presence of free fatty acids in the feedstock is a hindrance for this process as it leads to soap formation due to the reaction of hydroxide groups of alkali catalyst and free fatty acid groups. Many studies of two step processing have been reported where the acid value of the oil has been reduced by esterification step initially and then the processed oil further utilized in transesterification step (Joshi et al. 2017). The requirement of two steps makes the overall cost of production much higher. Also it is rather difficult to develop a commercial process which will effectively separate the glycerol from FAME produced especially in the presence of soap, which can be formed based on the free fatty acid content. Handling of chemical waste generated from neutralization of base catalyst is also a major problem.

Acid Catalyst

AAcid catalysts find less application as compared with the base catalysts due to their slower reaction rates. They are used mostly with feedstocks which have a high free fatty acid content as they catalyze the reaction of esterification and transesterification simultaneously as well as does not give processing problems in terms of soap formation. Study was reported with mixotrophic approach first to increase the lipid content in the microalgae (*C. protothecoides*) and further sulfuric acid was used as a catalyst in acidic transesterification reaction performed with methanol in excess at 56:1 molar ratio (Miao and Wu 2006). Study related to the comparison of the use of H_2SO_4 with HCl in transesterification reaction established that HCl gave 10% higher yield as compared to $_2SO_4$ (Kim et al. 2015). Commercial application of the use of acid catalyst is not economically feasible as it leads to generation of waste and higher temperature and pressure are required for the reaction and also the slower reaction rate, which leads to higher energy consumption. The longer reaction time with high temperature may also lead to corrosion of reactor due to the prolonged use of acidic conditions.

Enzymatic Catalyst

Enzyme-based transesterification process is an attractive alternative to the chemical catalysts. Enzymes can work under mild reaction conditions with low temperature and pressure requirement and can also tolerate the FFA and water in reaction mixture. Typically the important operating parameters as the pH of the reaction, concentration of enzymes, and substrates, and the interactive distance between substrate and enzyme plays crucial role in deciding the rates of reactions carried out using enzymes. Enzymes can be denatured and destabilized by excess methanol and glycerol present in the reaction mixture. Also the prices of enzymes are higher which hamper the process economics (Suali and Sarbatly 2012). To overcome the above-mentioned issues, the enzymes can be used after they are immobilized transforming the system into heterogeneous. Immobilization is carried out via adsorption, encapsulation, entrapment, and cross-linking. Adsorption is the oldest and most commonly used method as it is less expensive as compared to other available methods. Many studies have been reported for the use of immobilized lipase in transesterification reaction for production of biodiesel (Subhedar et al. 2015). The advantage of reusability also makes immobilized form a more feasible option as compared to the free form, though the mass transfer limitations need to be looked at due to the heterogeneous nature of system.

5.1.2 Catalytic Heterogeneous Transesterification

The heterogeneous solid catalysts are environmentally friendly as they are easily separable from reaction mixture and hence reusable. Easy separation of catalyst from reaction mixture with simple filtration helps in improving the process economics. Solid catalysts are further classified as solid acid catalyst and solid base catalyst. Solid acid catalyst includes resins, polyaniline sulfate, zeolite tungstated and sulfated zirconia, sulfated tin oxide, heteropolyacid, metal complexes, and acidic ionic liquids. Solid base catalyst includes calcium oxide, hydrotalcite (also called layered double hydroxide), zeolites, and alumina. Yield of 97.5% was reported for the biodiesel production from lipids extracted from *Nannochloropsis oculata* when Al_2O_3-supported CaO and MgO were used as catalysts under processing conditions of excess of methanol (1:30) and catalyst loading (80% w/w) required for the completion of reaction (Umdu et al. 2009). Use of Mg–Zr was proposed in one of the study performed where in situ and two-step processes were compared and single-step approach was found to be more efficient. Reaction was performed with a mixture of methanol and methylene dichloride in ratio of 3:1 with 10% w/v catalyst at 65 °C for 4 h and a yield of 28% of methyl esters was reported (Li et al. 2011b). A study on utilization of hierarchal zeolites in transesterification was performed to establish the specific form of zeolite that can yield highest conversion rate. From the study, H-beta zeolite was established to give higher conversion rates as compared to other zeolites (Carrero et al. 2011). Study was performed using KOH/La–Ba–Al_2O_3 as the heterogeneous catalyst for conversion

of microalgal lipids at 60 °C for 3 h with catalyst loading of 25% and the yield of biodiesel reported was 97.7% (Zhang et al. 2012). Syazwani et al. (2015) performed a study using CaO catalyst synthesized from angel wing shells in transesterification of N. oculata lipids. Yield of 84.1% was reported with 9% catalyst concentration and 1:150 molar ratio of lipids to methanol in a period of 1 h. Leaching of the heterogeneous catalyst into the final biodiesel product can be one of the concerns related to the use of these catalysts. There are many heterogeneous catalysts used for transesterification of edible oil and non-edible oil, but more thorough research needs to be performed for their application on microalgal lipids, as only limited information was observed in the literature for the algal lipids.

5.1.3 In situ Transesterification

In situ transesterification is the process where the extraction and transesterification reaction are carried out simultaneously. It has an advantage over conventional process as only a single step is required instead of two seperate steps of extraction and reaction. This approach of combination leads to intensification as it requires minimal amount of solvent, lesser reaction time, and easy separation of the products. The state of biomass is crucial in this approach as more amount of biodiesel is produced from dry biomass as compared to wet dry biomass.

Mechanically Catalyzed In situ Transesterification

The mechanically catalyzed in situ transesterification involves the use of mechanical processes based on the use of microwave (MW), ultrasound (US), and autoclave. These processes help in improving the surface area and local temperature of mixture leading to increased penetration of solvents to cells which further helps in enhanced extraction of lipids from microalgae. Microwave-assisted direct transesterification study was performed with dried *Nannochloropsis* and yield of 80.1% was reported under processing conditions of 1:12 (w/v) ratio of algae to methanol, 2% by weight KOH loading, and reaction time of 2–4 min at 60–65 °C (Patil et al. 2011a). Another study reported that with use of ultrasound, 91–96% yield was obtained in 20 min–2 h time with 1:105 to 1:315 algae to methanol molar ratio. The reaction time required for US is typically more as compared to MW (Ehimen et al. 2012), though the scale up prospects for MW need to be carefully evaluated.

Chemically Catalyzed In situ Transesterification

The chemically catalyzed reaction involves no use of mechanical energy. An important precondition of the chemical catalyst-based approach is that the process requires the use of dried biomass. Feedstock containing water more than 31.7% exhibit inhibition to transesterification reaction (Ehimen et al. 2010). These

reactions are mostly performed using co-solvent and ionic liquids. Co-solvents increase the efficiency of lipid extraction and increase the overall yield. In one of the study, hexane was used as the co-solvent and was supplemented with sulfuric acid and methanol. It was reported that the yield of biodiesel increased from 16.6 to 94.5% with an increase in hexane supplementation from 2 to 10 mL (Sangaletti-Gerhard et al. 2015). Comparison of chloroform and hexane as co-solvent established that chloroform increases the yield of biodiesel more than hexane (Kim et al. 2015). The use of co-solvent not only increases the yield but also reduces the requirement of methanol, facilitating the downstream processing. It has been reported in a study that the use of diethyl ether as a co-solvent reduced the requirement of methanol from 105:1 to 79:1 (Ehimen et al. 2012). Study to evaluate the transesterification reaction with different co-solvents (petroleum ether, chloroform, n-hexane, ethyl ether, carbon tetrachloride, n-butanol, and acetone) established that the highest ester yields were obtained with use of petroleum ether, chloroform, and n-hexane. The yield increased from 48.3% to above 90% when a co-solvent was used with ethanol clearly confirming the role of co-solvent (Zhang et al. 2015). Research has been also focused toward development of green solvents which will eliminate the harmful effects of conventional solvents (Jeevan Kumar et al. 2017). In recent years, the ionic liquids (salts in liquid form) have been utilized in biodiesel production. Ionic liquids come with advantages like high solubility, inherent basicity or acidity, negligible vapor pressure, and are recyclable. They also possess the ability to immobilize the catalysts (acid/basic), and this makes them easily separable and recyclable. Cost of the ionic liquids is the major drawback currently restricting their application in biodiesel production process especially considering the requirement at large scale. There are very few studies reported on the use of ionic liquids, and more research needs to be carried out for their application in biodiesel production from microalgae with a focus on reducing the requirement and maximizing the reuse during the processing.

5.2 Bioethanol

The biofuel which accounts for a significant fraction of the total production is bioethanol. Majority of it is produced from sugarcane and the remaining comes from other crops. Bioethanol from biomass is produced via fermentation or gasification process, and the availability of the feedstock depends upon the season and geographical conditions. Microalgae can be one of the potential feedstock for bioethanol production as they are able to produce starch and cellulose and also do not compete with the food crops for land and water. The production of bioethanol

from microalgae can be feasible on industrial scale when the method applied for hydrolysis is easy to handle, cost-effective, energy efficient, and maximum yield of reducing sugars is obtained. The absence of lignin makes the saccharification process easier and reduces the overall cost. Starch is stored by the microalgae inside the cells, and these cells can be separated periodically from photobioreactors and raceway ponds. Biomass harvested can be further disrupted, and starch extraction can be carried out via water or an organic solvent. Acids (concentrated and diluted) are mostly used for the disruption of the biomass. Zhou et al. (2011) reported that addition of 2.5% $MgCl_2$ in 2% HCl resulted in effective disruption and subsequent hydrolysis of the algal biomass, and 83% of the total sugars consisting of xylose, glucose, and arabinose were recovered via this process. Starch can also be saccharified using enzymes such as alpha amylase and gluco-amylase. Large amount of starch and glycogen have been reported to be present in microalgae like *Chlorella, Chlamydomonas, Dunaliella, Spirulina,* and *Scenedesmus* which can be processed for bioethanol production. The starch can be converted into ethanol with the step of anaerobic fermentation and pretreatment can be typically used to maximize the formation of sugars in first step and then ethanol in the second step. Study was performed using microalgal strains *M. afer* and *S. abundans* for bioethanol production, and it was reported from the study that dilute acid and cellulase-treated *S. abundans* was better feedstock yielding 0.103 g of ethanol per g of dry weight of microalgae. The process was optimized for sulfuric acid pretreatment, and 52% higher yield of ethanol was obtained with 10 mg/L microalgae using 3% v/v sulfuric acid treatment at 160 °C for 15 min (Guo et al. 2013).

The utilization of residual lipid extracted algae (LEA) for bioethanol production is also gaining attention in recent years. *Chlorococum* sp. was analyzed as a feedstock in a study to produce bioethanol. The lipid extraction was performed via supercritical method, and LEA was dried and further subjected to ethanol production giving a yield of 3.83 mg/L from 10 mg/L LEA (Harun et al. 2010). In another study, *C. vulgaris* FSP-E was reported to be used as biomass for bioethanol production with improvement based on pretreatment. Biomass was subjected to pretreatment using diluted acid and enzymes. It was reported that pretreatment with enzyme mixture of amylase/cellulase and dilute sulfuric acid were both effective techniques. The biomass was subjected to fermentation via SSF (simultaneous hydrolysis and fermentation) and SHF (separate hydrolysis and fermentation) processes. SHF process gave a higher ethanol yield of 11.66 mg/L as compared to SSF (Ho et al. 2013). El-Dalatony et al. (2016) performed a study on use of immobilized yeast and combination of sonication with enzymatic hydrolysis step. It was reported that sonication combined with hydrolysis gave higher yield of 445 mg/mg of total reducing sugars. Also it was reported that SSF gave higher ethanol

yield compared to SHF, and energy recovery of the process was improved due to use of immobilized yeast cells. Regenerated beads exhibited fermentation efficiency of 79.8% for four cycles. The treatment of algal biomass with CaO before the process of hydrolysis can also help in giving overall increase in reducing sugar yield (Khan et al. 2017). In one of the studies, utilization of mixed microalgae culture has been reported for bioethanol production. The effects of different pre-treatment strategies (acidic, alkaline, and enzymatic) were also studied, and it was reported that dilute sulfuric acid with $MgSO_4$ gave higher yield of reducing sugars as compared to only dilute sulfuric acid. Among all the processes employed, enzymatic process was reported to give the highest yield of reducing sugars (Shokrkar et al. 2017). The analysis of literature reveals that many approaches are available to optimize the process and maximize the ethanol yield with better utilization of the resources. A well designed approach with optimization studies for specific system need to be developed to facilitate the commercial scale application.

There is also a possible solution of genetic modification in the microalgae which can induce the direct production of ethanol from lifecycle of microalgae. The functional genetic diversity of microalgae is very large and can be utilized in developing specialized strains to directly produce bioethanol. The activity of pyruvate decarboxylase (PDC) and alcohol dehydrogenase (ADH) enzymes in the microalgae needs to be increased which will convert the fixed carbon into bioethanol. To modify the microalgae genetically, it will require more focused research and time. Currently, genetic modifications have made possible to increase the carbohydrate accumulation in microalgae (Silva and Bertucco 2016), and hence it definitely offers as a possibility even for direct ethanol production.

5.3 Biogas

Biogas production is an anaerobic process in which a gas is generated by decomposition of organic materials with the help of specialized organisms. Biogas mainly consists of methane (55–75%) and carbon dioxide (25–45%) with other constituents like H_2, N_2, water vapor, and H_2S in minor fractions. The production process consists of stages like hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Microalgae can also be a potential feedstock for biogas production, more promising than the utilization in other forms of biofuels due to the energy efficiency of the process for biogas. There is no requirement of lipid extraction process and the product, that is, biogas obtained in gaseous form does not require any separation. All the macromolecules present in the microalgae are typically utilized for the biogas fermentation process. The raw microalgae as well as the residuals from the

other biofuels production process can be used in biogas production process. The factors affecting biogas production consist of retention time, organic loading, pH, temperature, quality of the substrates (characteristic of cell wall), pretreatment of substrate, and the presence of methanogenesis inhibitors (Jankowska et al. 2017). The digestibility of cell wall can be improved with the help of pretreatment which further increase the biogas yield and help in intensification of the process. The different pretreatment processes include mechanical (ultrasound, high pressure homogenization, and microwave), thermal, chemical (use of alkali, acids, and ionic liquids), and biological (enzymes). Ultrasound pretreatment can increase the methane yield by up to 91% (Park et al. 2013). Microwave irradiation also has an effect on the cell wall protein which results in the disruption of the cells leading to easy access to the cellular material. Irradiation of microalgae with MW has been reported to increase the production of biogas up to 79% (Passos et al. 2013). Microwave irradiation can be a efficient technique for pretreatment as the pretreatment time required is less but high energy requirements might be an issue when employed on large scale. Thermal pretreatment of microalgae cells is typically performed using autoclaves, heat chambers, or water bath. González-Fernández et al. (2012a) reported an increase in biogas yield by 123% with help of thermal pretreatment. Disadvantage of this method is it consumes large amount energy but the energy available after heating can be employed to maintain the temperature of reactor during anaerobic fermentation and hence some heat integration approaches can be thought of. Enzymes (mostly cellulase) can also be employed in biological pretreatment of microalgae as they are rich in cellulose. The lipid extraction efficiency can be increased by up to 56% with help of enzymes (Fu et al. 2010). Cost of enzymes is the major hindrance in the use of enzymes in pretreatment process. Acid and alkali pretreatment come under the category of chemical pretreatment which mostly uses sulfuric acid as the acid and sodium hydroxide as the alkali. With the chemical pretreatment, the biogas yield can be increased by threefold to fourfold (Jankowska et al. 2017). The summary of effects of different pretreatment processes on biogas production has been reported in Table 3. Combinations of pretreatment process like employing dilute acid pretreatment with microwave or ultrasound-assisted approach can further result in significant increase in biogas yield. Such combined processes also help in reduction of process cost and overcome the disadvantages of individual methods.

Table 3 Different methods employed for pretreatment of microalgae

Strain	Processing conditions	Method of pretreatment	Operating conditions	Biogas production		Reference
				Before pretreatment	After pretreatment	
Nannochloropsis salina	40 days (38 °C)	Freezing overnight	−15 °C, overnight	0.347 L biogas/g VS	0.233 L biogas/g VS	Schwede et al. (2011)
		Thermal	100 °C, 8 h		0.549 L biogas/g VS	
		Microwave	5 × until boiling at 600 W, 2450 MHz		0.487 L biogas/g VS	
		Ultrasound	3 × 45 s at 200 W, 30 kHz		0.274 L biogas/g VS	
		French Press	2 × 10 MPa		0.460 L biogas/g VS	
Spirulina maxima	60 days (35 °C)	Ultrasound	10 min (polytron generator)	0.19 L CH_4/g VS	0.17 L CH_4/g VS	Samson and Leduy (1983)
		Thermo-chemical	50 °C (1 h in water bath)		0.21 L CH_4/g VS	
			100 °C (1 h water bath)		0.22 L CH_4/g VS	
			150 °C (1 h in steam sterilizer)		0.24 L CH_4/g VS	
Scenedesmus sp.	34 days (35 °C)	Thermal	70 °C, 25 min	0.082 L CH_4/g COD	0.089 L CH_4/g COD	González-Fernández et al. (2012b)
			80 °C, 25 min		0.129 L CH_4/g COD	
		Ultrasound	130 MJ/kg, 30 min		0.154 L CH_4/g COD	

(continued)

Table 3 (continued)

Strain	Processing conditions	Method of pretreatment	Operating conditions	Biogas production		Reference
				Before pretreatment	After pretreatment	
Rhizoclonium	28 days (53 °C)	Size reduction (cutting)	5 cm, 1 cm	0.23–0.24 L CH_4/g TS	0.093–0.100 L CH_4/g TS	Ehimen et al. (2013)
		Size reduction (grinding)	<0.1 mm		0.100–0.113 L CH_4/g TS	
		Sonication	20 kHz, 10 min		0.113–0.127 L CH_4/g TS	
		Enzymes	Combination of enzymes (lipase, xylanase, α-amylase, protease, cellulase)		0.143 L CH_4/g TS	
Microalgal biomass	HRT 15 days (35 °C)	Microwave	900 W, t = 3 min, 110 °C, 200 kJ/kg VS	0.13 L CH_4/g VS	0.17 L CH_4/g VS	Passos et al. (2014)
	20 days (35 °C)			0.17 L CH_4/g VS	0.27 L CH_4/g VS	
Algae biomass	28 days (38 °C)	Thermal	100 °C, 8 h	0.34 g MSGP g/L	0.45 MSGP g/L	Chen and Oswald (1998)
Chlorella vulgaris	25 days (35 °C)	Ultrasound	200 J/mL	0.230 L CH_4/g VS	0.440 L CH_4/g VS	Park et al. (2013)
Scenedesmus obliquus, Chlorella vulgaris	46 days (35 °C)	Microwave	21,800 kJ/kg TS	0.172 L biogas/g VS	0.2120 L biogas/g VS	Passos et al. (2013)
			43,600 kJ/kg TS		0.245 L biogas/g VS	
			65,400 kJ/kg TS		0.307 L biogas/g VS	

(continued)

Table 3 (continued)

Strain	Processing conditions	Method of pretreatment	Operating conditions	Biogas production		Reference
				Before pretreatment	After pretreatment	
Isochrysis galbana	15 days (30 °C)	Mechanical	Stirring with 1 g of glass beads, 1 min	22 mL of biogas	12.7 mL of biogas	Santos et al. (2014)
		Chemical	40 °C, 0.2% v/v acid, t = 16 h		26 mL of biogas	
		Thermal	60 °C, 16 h		3.7 mL of biogas	
		Thermal	40 °C, 16 h		3.0 mL of biogas	
Scenedesmus	35 days (38 °C)	Lipid extraction	In hexane, Soxhlet apparatus, 6 h,	0.18 L CH_4/g VS	0.33 L CH_4/g VS	Keymer et al. (2013)
		High pressure thermal hydrolysis	170 °C, 800 kPa, 30 min		0.24 L CH_4/g VS	
		LE and HPTH			0.38 L CH_4/g VS	

MSGP methane specific gas production, *VS* volatile solids, *LE* Lipid extracted, *HPTH* high pressure thermal hydrolysis

6 Analysis of Reactor Configurations for Process Intensification

Biodiesel production from microalgae has been quite successful under laboratory scales and can be under serious consideration for commercialization. The biodiesel production can also be significantly improved based on the concept of process intensification that focuses on achieving shorter reaction time and high conversion with lower molar ratio of alcohol to oil and low catalyst concentration, also possibly giving lower operating cost and energy consumption for biodiesel purification with recovery of glycerol, catalyst, and excess alcohol. Reactor configurations which can be utilized for intensification of biodiesel production process are now discussed.

6.1 Cavitational Reactors

Application of cavitation in the field of biodiesel production has gained interest lately. Cavitation helps the reaction by providing mechanical energy for mixing and enhanced surface area for the transesterification reaction resulting in reduced reaction time and increased yield (Gogate and Pandit 2004). The main effects which are generated due to cavitation consist of (1) chemical effect which is produced due to generation of radicals (H^+, OH^-, and HO_2^+) from transient implosive collapse of the bubbles though this is not dominating in the case of biofuel production, (2) homogenization of the mixture, which is caused by micro-turbulence generated due to the collapse of bubbles. Due to the formation of fine emulsion, the interfacial region is increased between oil and alcohol which leads to increased reaction rate and high yield. There are mainly two types of cavitational reactors, ultrasonic (US) and hydrodynamic (HC). The ultrasonic reactors are operated in the frequency range of 20–40 kHz with lower range of power (120–220 W) (Gupta and Verma 2015), giving dominant physical effects controlling biodiesel production. Utilization of 40 kHz frequency has been reported to reduce the time required for reaction drastically (Stavarache et al. 2005). Ultrasound-assisted transesterification reactions are generally performed with reaction parameters as: molar ratio (1:6–1:10), catalyst loading (0.5–2 wt% of oil), and reaction time (15–20 min) with temperature over the range of 30 to 60 °C as observed in the literature (Gole and Gogate 2012). It is important to understand that most of the applications have been based on the use of ultrasonic horn and bath at the laboratory scale but application of ultrasound on continuous mode has not been reported. More research needs to be performed to utilize ultrasound effectively at commercial scale especially using continuous operation. Hydrodynamic cavitation (HC) produces similar effects to that of ultrasonic cavitation; only difference is in the method of generation of cavities. Cavity generation is due to sudden pressure drop with help of constriction introduced in the flow of the liquid. These reactors are generally more energy efficient and can work with large quantity reaction batch as compared to US and

with similar reaction parameters as that of US but the reaction time required may be higher (45–60 min) than US (Ghayal et al. 2013). It is important to understand that the cavitational yield (amount of product per unit energy) of HC is also typically higher than US.

6.2 Microreactors

Miniature reaction systems have proven to provide sustainable and innovative solutions and have been utilized at both laboratory level and industrial level with good degree of intensification benefits. Intensified heat and mass transfer are achieved with these reactors as they have a small characteristic dimension and high surface-to-volume ratio offering proper temperature control. Immiscible liquid–liquid reactions can be carried out with higher efficiency with this reactor as it provides very high interfacial area between phases which further improves the rate of mass transfer (Kashid and Kiwi-Minsker 2009). Transesterification reaction consists of two immiscible reactants, that is, triglycerides and methanol. There are reports in which homogenous transesterification reaction have been performed using microreactor with significant reduction in reaction time (Mazubert et al. 2013; Wen et al. 2009). Typical operating conditions consist of methanol-to-oil molar ratio at 1:4–1:9 and catalyst loading in the range of 1–4.5% w/w of oil with a flow rate varied from 8 to 15 mL/h which can give yield of biodiesel up to 99% in very less reaction time of 1–6 min. More work is required to be performed to establish the design and scale up strategies for application of micro-reactors at the commercial scale of operation for the specific application of biofuel production from microalgae.

6.3 Microwave Reactor

Microwave reactors work on the principle of intensification based on the effects of dipolar polarization and ionic conduction. The dipolar polarization occurs when the alignment of the dipoles occurs in the direction of electric field imposed with help of microwave irradiation. Oscillation of the charged dissolved particles due to microwave results in the ionic conduction. Transesterification reaction performed using these reactors shows significant increase in reaction rate. Also it has been reported that intensification in the transesterification reaction is more sensitive for the use of methanol than ethanol due to low gyration radius and molecular inertia (Terigar et al. 2010). Intensification trends have been reported with different heterogeneous and homogenous transesterification reactions for the use of microwave reactors (Mazubert et al. 2013). It can be seen from the studies reported in the literature that the important reaction parameters are molar ratio (1:6–1:12), catalyst loading (0.15– 5 wt% of oil), temperature (40–60 °C), and power (300–1600 W) with required reaction time varying from 0.5 to 20 min.

6.4 Oscillatory Baffled Reactor

Oscillatory baffled reactor (OBR) consists of equally spaced orifice plate baffles arranged in a tube operating with an oscillatory or pulsed flow with generation of re-circulating flow pattern. This reactor provides enhanced mixing and inter-phase contact within sufficiently long residence time suitable for the reaction when employed in transesterification reaction. It can be established from the data available on transesterification reaction with OBR that the molar ratio in the range of 1:6–1:9 with flow rate of 0.12–3.12 L/h and residence time ranging from 20 to 40 min is able to yield 99% conversion in almost all the studies (Harvey et al. 2003; Zheng et al. 2007). OBR can also work with heterogeneous system and their scale up for effective operation at commercial scale is possible. It is important to understand that no direct work has been still reported for utilization of algal oil in biodiesel production with OBR, though the reported trends for other similar systems do induce a confidence for possible success.

6.5 Reactive Distillation

Reactive distillation (RD) combines the chemical reaction and product separation in a single unit. RD column boosts the conversion with improvement in selectivity by breaking the reaction equilibrium conditions (Estrada-Villagrana et al. 2006). The application of this reactor in biodiesel production can be very helpful as demonstrated by He et al. (2006). In the study, the canola oil and methanol feed were made to enter through an in-line static mixer into the RD column. Downward flow of reactant from the top of the RD column across the plate ensured efficient contact with vapors of methanol (produced in reboiler from product mixture) providing uniform mixing at each plate. Virtually, a series of "mini- reactors" were created in the reaction zone of RD column. Methanol from the distillate could be recycled and was combined with the feed methanol and then refluxed back to the RD column. This made the reactor to give 94.4% of yield with methanol: oil molar ratio of 4:1. From this study, it was also established that there is drastic decrease in quantity of methanol required and reaction time as compared to the conventional reactors. The requirement of extra unit operation required for recovery of solvent is also not present in RD giving lower capital costs. It is important to understand that not much work could be seen for the use of algal oil in the reactive distillation approach. More investigation needs to be carried out to employ this reactor for the algal oil with a detailed study on parameter optimization and also establish scale up strategies so that the commercial-scale biodiesel production from algal oil is a possibility.

6.6 Centrifugal Contact Separator

Centrifugal contact separator (CCS) employs the chemical reaction, and centrifugal separation in a single apparatus. Preheated oil is fed into the reactor, and the reaction is started by adding the methanol and the catalyst. The dispersion of the immiscible liquids takes place in the annular gap between the static housing and the rotating centrifuge. Further this mixture is transferred to the hollow centrifuge through a hole at bottom and separation into heavy and light layers take place via centrifugation. The optimum conditions reported by Kraai et al. (2009) for this system, though not for algal oil, were rotational frequency of 30 Hz, oil flow rate at 12.6 mL/min, sodium methoxide catalyst concentration of 1% w/w of oil, and reaction temperature of 75 °C. The FAME yield of 96% was reported in time period of 30 min. It was also reported that further increase in temperature and catalyst beyond optimum leads to excessive evaporation of methanol and soap formation which affects the overall reaction rates. The higher flow rates of oil also were reported to have a negative effect on the mean residence time of mixture lowering the yield of FAME. Again similar to the reactive distillation, more investigations are needed for the application of centrifugal contact separators for the specific feed stock of algal oil before firm conclusion can be made.

6.7 Membrane Reactor

In order to overcome the limitations of conventional biodiesel production processes, the development of membrane reactor can be a potential solution. Reaction and separation occur in a single chamber, and this ensures that the reversible reaction proceeds in the forward path with efficient removal of desired products from reaction mixture which leads to increase in yield (Cao et al. 2008, 2007; Dube et al. 2007). Membrane reactor works on the principle of utilizing the immiscibility of methanol with oil and miscibility of products (FAME and glycerol) in methanol. During the transesterification process, oil exists in the form of emulsion in methanol and reaction occurs at the surface of oil droplets. FAME produced via transesterification is soluble in methanol and is able to pass through the membrane with the by-product glycerol. The oil droplets being larger in size cannot pass through the membrane and remain in the reactor vessel. The simultaneous removal of product from a reversible reaction helps in the improvement of the reaction rates, and the permeate obtained is in pure form which requires less processing. Cao et al. (2008) have investigated the transesterification reaction using different feedstocks (soybean oil, canola oil, a hydrogenated palm oil/palm oil blend, yellow grease, and brown grease) having varied FFA presence. With efficient purification and separation process, membrane reactor was demonstrated to give high efficacy for different feedstocks making it a energy efficient, and environmental friendly reactor.

From the above-mentioned reactor configurations for process intensification, it can be said that the ultrasound and microwave reactors have been already employed for biodiesel production from microalgae as the feedstock and remaining need to be utilized via process intensification study to make process economically feasible. As mentioned in Sect. 5.2 and 5.3, microwave- and ultrasound-assisted processes have also been employed in enhanced bioethanol and biogas production from microalgae. It can be concluded that the study on US and MW is quite progressive as compared to other technologies available and more research needs to be performed for establishment of other available technologies in biodiesel production from microalgae as they might have a potential to overcome the disadvantages of US and MW, especially at large scale of operation.

7 Conclusions

Biofuels produced from microalgae can be considered as an effective alternative to petrochemical fuels but there are limited technologies available currently which can be commercially applied. Application of process intensification approaches at different stages of processing can give an energy efficient process with scope for commercialization as demonstrated in the current chapter. The techniques involved in harvesting as the very first stage of processing and subsequent lipid extraction need to be developed into efficient techniques based on process intensification to achieve economic feasibility of process. Innovative solutions are also required to build strategies for the subsequent reactions and separations which will give a possible solution maintaining the positive aspects of current methods and remove the undesired ones which will make the process costeffective and give positive energy gains. The development of microalgae biorefinery can be a feasible solution as high-value products which can be beneficial to the cosmetics, pharmaceutical, and nutritional industries remain largely unexplored, and this will essentially shift the current focus from only biofuels production to diversification of the other products with biofuels. The processes developed must be applicable to the microalgal species which are available commonly and should be easily transformed into continuous mode which can be applicable on commercial scale. Process intensification can help to improve the working of current processes making them efficient in aspects of time and energy. It has been established from the research articles available that biodiesel from microalgae is more feasible as compared to bioethanol and biogas. Biogas and bioethanol production from microalgae can also be improved via process intensification techniques like ultrasound and microwave with benefits as lower times, lower requirement of reactants, and lower temperature. Overall, it can be concluded that microalgae can be a potential feedstock for production of biofuels (biodiesel, bioethanol, and biogas) at commercial scale and process intensification aspects can be integrated to give production at lower cost and energy.

References

Abbott, M. S. R., Brain, C. M., Harvey, A. P., Morrison, M. I., & Valente, G. (2015). Liquid culture of microalgae in a photobioreactor (PBR) based on oscillatory baffled reactor (OBR) technology—A feasibility study. *Chemical Engineering Science, 138,* 315–323.

Adam, F., Abert-Vian, M., Peltier, G., & Chemat, F. (2012). "Solvent-free" ultrasound-assisted extraction of lipids from fresh microalgae cells: A green, clean and scalable process. *Bioresource Technology, 114,* 457–465.

Ahmed, M. B., Zhou, J. L., Ngo, H. H., Guo, W., Thomaidis, N. S., & Xu, J. (2017). Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review. *Journal of Hazardous Materials, 323,* 274–298.

Aslan, S., & Kapdan, I. K. (2006). Batch kinetics of nitrogen and phosphorus removal from synthetic wastewater by algae. *Ecological Engineering, 28,* 64–70.

Bilad, M. R., Discart, V., Vandamme, D., Foubert, I., Muylaert, K., & Vankelecom, I. F. J. (2013). Harvesting microalgal biomass using a magnetically induced membrane vibration (MMV) system: Filtration performance and energy consumption. *Bioresource Technology, 138,* 329–338.

Cao, P., Dubé, M. A., & Tremblay, A. Y. (2008). Methanol recycling in the production of biodiesel in a membrane reactor. *Fuel, 87,* 825–833.

Cao, P., Tremblay, A. Y., Dubé, M. A., & Morse, K. (2007). Effect of membrane pore size on the performance of a membrane reactor for biodiesel production. *Industrial and Engineering Chemistry Research, 46,* 52–58.

Carrero, A., Vicente, G., Rodríguez, R., Linares, M., & Del Peso, G. L. (2011). Hierarchical zeolites as catalysts for biodiesel production from Nannochloropsis microalga oil. *Catalysis Today, 167,* 148–153.

Carvalho, A. P., Meireles, L. A., & Malcata, F. X. (2006). Microalgal reactors: A review of enclosed system designs and performances. *Biotechnology Progress, 22,* 1490–1506. https://doi.org/10.1021/bp060065r.

Chen, P. H., & Oswald, W. J. (1998). Thermochemical treatment for algal fermentation. *Environment International, 24,* 889–897.

Choudhary, P., Prajapati, S. K., Kumar, P., Malik, A., & Pant, K. K. (2017). Development and performance evaluation of an algal biofilm reactor for treatment of multiple wastewaters and characterization of biomass for diverse applications. *Bioresource Technology, 224,* 276–284.

Dube, M. A., Tremblay, A. Y., & Liu, J. (2007). Biodiesel production using a membrane reactor. *Bioresource Technology, 98,* 639–647.

Ehimen, E. A., Holm-Nielsen, J. B., Poulsen, M., & Boelsmand, J. E. (2013). Influence of different pre-treatment routes on the anaerobic digestion of a filamentous algae. *Renewable Energy, 50,* 476–480.

Ehimen, E. A., Sun, Z. F., & Carrington, C. G. (2010). Variables affecting the in situ transesterification of microalgae lipids. *Fuel, 89,* 677–684.

Ehimen, E. A., Sun, Z., & Carrington, G. C. (2012). Use of ultrasound and co-solvents to improve the in-situ transesterification of microalgae biomass. *Procedia Environmental Sciences, 15,* 47–55. https://doi.org/10.1016/j.proenv.2012.05.009.

El-Dalatony, M. M., Kurade, M. B., Abou-Shanab, R. A. I., Kim, H., Salama, E. S., & Jeon, B. H. (2016). Long-term production of bioethanol in repeated-batch fermentation of microalgal biomass using immobilized *Saccharomyces cerevisiae*. *Bioresource Technology, 219,* 98–105.

Estrada-Villagrana, A. D., Quiroz-Sosa, G. B., Jiménez-Alarcón, M. L., Alemán-Vázquez, L. O., & Cano-Domínguez, J. L. (2006). Comparison between a conventional process and reactive distillation for naphtha hydrodesulfurization. *Chemical Engineering and Processing: Process Intensification, 45,* 1036–1040.

Ferreira, A. F., Dias, A. P. S., Silva, C. M., & Costa, M. (2016). Effect of low frequency ultrasound on microalgae solvent extraction: Analysis of products, energy consumption and emissions. *Algal Research, 14,* 9–16.

Fu, C. C., Hung, T. C., Chen, J. Y., Su, C. H., & Wu, W. T. (2010). Hydrolysis of microalgae cell walls for production of reducing sugar and lipid extraction. *Bioresource Technology, 101,* 8750–8754.

Gao, S., Yang, J., Tian, J., Ma, F., Tu, G., & Du, M. (2010). Electro-coagulation-flotation process for algae removal. *Journal of Hazardous Materials, 177,* 336–343.

Gendy, T. S., & El-Temtamy, S. A. (2013). Commercialization potential aspects of microalgae for biofuel production: An overview. *Egyptian Journal of Petroleum, 22,* 43–51.

Ghayal, D., Pandit, A. B., & Rathod, V. K. (2013). Optimization of biodiesel production in a hydrodynamic cavitation reactor using used frying oil. *Ultrasonics Sonochemistry, 20,* 322–328.

Gogate, P. R., & Pandit, A. B. (2004). Sonochemical reactors: Scale up aspects. *Ultrasonics Sonochemistry, 11,* 105–117.

Gole, V. L., & Gogate, P. R. (2012). Intensification of synthesis of biodiesel from nonedible oils using sonochemical reactors. *Industrial and Engineering Chemistry Research*, *51*(37), 11866–11874.

González-Fernández, C., Sialve, B., Bernet, N., & Steyer, J. P. (2012a). Thermal pretreatment to improve methane production of *Scenedesmus* biomass. *Biomass and Bioenergy, 40,* 105–111.

González-Fernández, C., Sialve, B., Bernet, N., & Steyer, J. P. (2012b). Comparison of ultrasound and thermal pretreatment of *Scenedesmus* biomass on methane production. *Bioresource Technology, 110,* 610–616.

Guo, H., Daroch, M., Liu, L., Qiu, G., Geng, S., & Wang, G. (2013). Biochemical features and bioethanol production of microalgae from coastal waters of Pearl River Delta. *Bioresource Technology, 127,* 422–428.

Gupta, A., & Verma, J. P. (2015). Sustainable bio-ethanol production from agro-residues: A review. *Renewable and Sustainable Energy Reviews, 41,* 550–567.

Han, F., Pei, H., Hu, W., Jiang, L., Cheng, J., & Zhang, L. (2016). Beneficial changes in biomass and lipid of microalgae *Anabaena variabilis* facing the ultrasonic stress environment. *Bioresource Technology, 209,* 16–22.

Harun, R., Danquah, M. K., & Forde, G. M. (2010). Microalgal biomass as a fermentation feedstock for bioethanol production. *Journal of Chemical Technology and Biotechnology, 85,* 199–203.

Harvey, A. P., Mackley, M. R., & Seliger, T. (2003). Process intensification of biodiesel production using a continuous oscillatory flow reactor. *Journal of Chemical Technology and Biotechnology, 78,* 338–341.

He, B. B., Singh, A. P., & Thompson, J. C. (2006). A novel continuous-flow reactor using reactive distillation for biodiesel production. *Transactions of the ASABE, 49,* 107–112.

Ho, S. H., Huang, S. W., Chen, C. Y., Hasunuma, T., Kondo, A., & Chang, J. S. (2013). Bioethanol production using carbohydrate-rich microalgae biomass as feedstock. *Bioresource Technology, 135,* 191–198.

Jankowska, E., Sahu, A. K., & Oleskowicz-Popiel, P. (2017). Biogas from microalgae: Review on microalgae's cultivation, harvesting and pretreatment for anaerobic digestion. *Renewable and Sustainable Energy Reviews, 75,* 692–709.

Jeevan Kumar, S. P., Vijay Kumar, G., Dash, A., Scholz, P., & Banerjee, R. (2017). Sustainable green solvents and techniques for lipid extraction from microalgae: A review. *Algal Research, 21,* 138–147.

Joshi, S., Gogate, P. R., Moreira, P. F., & Giudici, R. (2017). Intensification of biodiesel production from soybean oil and waste cooking oil in the presence of heterogeneous catalyst using high speed homogenizer. *Ultrasonics Sonochemistry, 39,* 645–653.

Kashid, M. N., & Kiwi-Minsker, L. (2009). Microstructured reactors for multiphase reactions: State of the art. *Industrial and Engineering Chemistry Research, 48,* 6465–6485.

Keymer, P., Ruffell, I., Pratt, S., & Lant, P. (2013). High pressure thermal hydrolysis as pre-treatment to increase the methane yield during anaerobic digestion of microalgae. *Bioresource Technology, 131,* 128–133.

Khan, M. I., Lee, M. G., Shin, J. H., & Kim, J. D. (2017). Pretreatment optimization of the biomass of *Microcystis aeruginosa* for efficient bioethanol production. *AMB Express, 7,* 19.

Kim, B., Im, H., & Lee, J. W. (2015). In situ transesterification of highly wet microalgae using hydrochloric acid. *Bioresource Technology, 185,* 421–425.

Kim, J., Yoo, G., Lee, H., Lim, J., Kim, K., Kim, C. W., et al. (2013). Methods of downstream processing for the production of biodiesel from microalgae. *Biotechnology Advances, 31,* 862–876.

Kraai, G. N., Schuur, B., van Zwol, F., van de Bovenkamp, H. H., Heeres, H. J. (2009). Novel highly integrated biodiesel production technology in a centrifugal contactor separator device. *Chemical Engineering Journal*, *154*, 384–389. https://doi.org/10.1016/j.cej.2009.04.047.

Lee, Y., & Li, P. (2016). Using resonant ultrasound field-incorporated dynamic photobioreactor system to enhance medium replacement process for concentrated microalgae cultivation in continuous mode. *Chemical Engineering Research and Design, 118,* 112–120.

Lee, K. T., Lim, S., Pang, Y. L., Ong, H. C., & Chong, W. T. (2014). Integration of reactive extraction with supercritical fluids for process intensification of biodiesel production: Prospects and recent advances. *Progress in Energy and Combustion Science, 45,* 54–78.

Lee, J. Y., Yoo, C., Jun, S. Y., Ahn, C. Y., & Oh, H. M. (2010). Comparison of several methods for effective lipid extraction from microalgae. *Bioresource Technology, 101,* S75–S77.

Li, Y., Chen, Y. F., Chen, P., Min, M., Zhou, W., Martinez, B., et al. (2011a). Characterization of a microalga *Chlorella* sp. well adapted to highly concentrated municipal wastewater for nutrient removal and biodiesel production. *Bioresource Technology, 102,* 5138–5144.

Li, Y., Lian, S., Tong, D., Song, R., Yang, W., Fan, Y., et al. (2011b). One-step production of biodiesel from *Nannochloropsis* sp. on solid base Mg–Zr catalyst. *Applied Energy, 88,* 3313–3317.

Lu, W., Wang, Z., Wang, X., & Yuan, Z. (2015). Cultivation of *Chlorella* sp. using raw diary wastewater for nutrient removal and biodiesel production: Characteristics comparison of indoor bench-scale and outdoor pilot-scale cultures. *Bioresource Technology, 192,* 382–388.

Mazubert, A., Poux, M., & Aubin, J. (2013). Intensified processes for FAME production from waste cooking oil: A technological review. *Chemical Engineering Journal, 233,* 201–223.

Miao, X., & Wu, Q. (2006). Biodiesel production from heterotrophic microalgal oil. *Bioresource Technology, 97,* 841–846.

Misra, R., Guldhe, A., Singh, P., Rawat, I., Stenstrom, T. A., & Bux, F. (2015). Evaluation of operating conditions for sustainable harvesting of microalgal biomass applying electrochemical method using non sacrificial electrodes. *Bioresource Technology, 176,* 1–7.

Olguín, E. J. (2012). Dual purpose microalgae-bacteria-based systems that treat wastewater and produce biodiesel and chemical products within a biorefinery. *Biotechnology Advances, 30,* 1031–1046.

Park, K. Y., Kweon, J., Chantrasakdakul, P., Lee, K., & Cha, H. Y. (2013). Anaerobic digestion of microalgal biomass with ultrasonic disintegration. *International Biodeterioration & Biodegradation, 85,* 598–602.

Passos, F., Hernández-Mariné, M., García, J., Ferrer, I. (2014). Long-term anaerobic digestion of microalgae grown in HRAP for wastewater treatment. Effect of microwave pretreatment. *Water Research, 49*.

Passos, F., Sole, M., Garcia, J., & Ferrer, I. (2013). Biogas production from microalgae grown in wastewater: Effect of microwave pretreatment. *Applied Energy, 108,* 168–175.

Patel, A., Gami, B., Patel, P., Patel, B. (2016). Microalgae: Antiquity to era of integrated technology. *Renewable and Sustainable Energy Reviews*. https://doi.org/10.1016/j.rser.2016.12.081.

Patil, P. D., Gude, V. G., Mannarswamy, A., Cooke, P., Munson-McGee, S., Nirmalakhandan, N., et al. (2011a). Optimization of microwave-assisted transesterification of dry algal biomass using response surface methodology. *Bioresource Technology, 102,* 1399–1405.

Patil, P. D., Gude, V. G., Mannarswamy, A., Deng, S., Cooke, P., Munson-McGee, S., et al. (2011b). Optimization of direct conversion of wet algae to biodiesel under supercritical methanol conditions. *Bioresource Technology, 102,* 118–122.

Pfaffinger, C. E., Schöne, D., Trunz, S., Löwe, H., & Weuster-Botz, D. (2016). Model-based optimization of microalgae areal productivity in flat-plate gas-lift photobioreactors. *Algal Research, 20,* 153–163.

Prabakaran, P., & Ravindran, A. D. (2011). A comparative study on effective cell disruption methods for lipid extraction from microalgae. *Letters in Applied Microbiology, 53,* 150–154.

Priyadarshani, I., & Rath, B. (2012). Commercial and industrial applications of micro algae—A review. *Journal of Algal Biomass Utilization, 3,* 89–100.

Rodolfi, L., Zittelli, G. C., Bassi, N., Padovani, G., Biondi, N., Bonini, G., et al. (2009). Microalgae for oil: Strain selection, induction of lipid synthesis and outdoor mass cultivation in a low-cost photobioreactor. *Biotechnology and Bioengineering, 102,* 100–112.

Samson, R., & Leduy, A. (1983). Influence of mechanical and thermochemical pretreatments on anaerobic digestion of *Spirulina maxima* algal biomass. *Biotechnology Letters, 5,* 671–676.

Sangaletti-Gerhard, N., Cea, M., Risco, V., & Navia, R. (2015). In situ biodiesel production from greasy sewage sludge using acid and enzymatic catalysts. *Bioresource Technology, 179,* 63–70.

Santos, N. O., Oliveira, S. M., Alves, L. C., & Cammarota, M. C. (2014). Methane production from marine microalgae *Isochrysis galbana*. *Bioresource Technology, 157,* 60–67.

Schuchardt, U., Sercheli, R., & Matheus, R. (1998). Transesterification of vegetable oils: A review general aspects of transesterification of vegetable oils acid-catalyzed processes base-catalyzed processes. *Journal of the Brazilian Chemical Society, 9,* 199–210.

Schwede, S., Kowalczyk, A., Gerber, M., Span, R. (2011). Influence of different cell disruption techniques on mono digestion of algal biomass. In *Bioenergy Technology—World Renewable Energy Congress* (pp. 41–47). https://doi.org/10.3384/ecp1105741.

Sebestyen, P., Blanken, W., Bacsa, I., Toth, G., Martin, A., Bhaiji, T., et al. (2016). Upscale of a laboratory rotating disk biofilm reactor and evaluation of its performance over a half-year operation period in outdoor conditions. *Algal Research, 18,* 266–272.

Shokrkar, H., Ebrahimi, S., & Zamani, M. (2017). Bioethanol production from acidic and enzymatic hydrolysates of mixed microalgae culture. *Fuel, 200,* 380–386.

Silva, C. E. F., & Bertucco, A. (2016). Bioethanol from microalgae and cyanobacteria: A review and technological outlook. *Process Biochemistry, 51,* 1833–1842.

Solovchenko, A., Pogosyan, S., Chivkunova, O., Selyakh, I., Semenova, L., Voronova, E., et al. (2014). Phycoremediation of alcohol distillery wastewater with a novel *Chlorella sorokiniana* strain cultivated in a photobioreactor monitored on-line via chlorophyll fluorescence. *Algal Research, 6,* 234–241.

Stavarache, C., Vinatoru, M., Nishimura, R., & Maeda, Y. (2005). Fatty acids methyl esters from vegetable oil by means of ultrasonic energy. *Ultrasonics Sonochemistry, 12,* 367–372.

Suali, E., & Sarbatly, R. (2012). Conversion of microalgae to biofuel. *Renewable and Sustainable Energy Reviews, 16,* 4316–4342.

Subhedar, P. B., Botelho, C., Ribeiro, A., Castro, R., Pereira, M. A., Gogate, P. R., et al. (2015). Ultrasound intensification suppresses the need of methanol excess during the biodiesel production with lipozyme TL-IM. *Ultrasonics Sonochemistry, 27,* 530–535.

Suresh Kumar, K., Dahms, H. U., Won, E. J., Lee, J. S., & Shin, K. H. (2015). Microalgae—A promising tool for heavy metal remediation. *Ecotoxicology and Environmental Safety, 113,* 329–352.

Syazwani, O., Rashid, U., & Taufiq Yap, Y. H. (2015). Low-cost solid catalyst derived from waste *Cyrtopleura costata* (Angel Wing Shell) for biodiesel production using microalgae oil. *Energy Conversion and Management, 101,* 749–756.

Takagi, M., Karseno, Yoshida, T. (2006). Effect of salt concentration on intracellular accumulation of lipids and triacylglyceride in marine microalgae Dunaliella cells. *Journal of Bioscience and Bioengineering, 101*, 223–226.

Terigar, B. G., Balasubramanian, S., Lima, M., & Boldor, D. (2010). Transesterification of soybean and rice bran oil with ethanol in a continuous-flow microwave-assisted system: Yields, quality, and reaction kinetics. *Energy & Fuels, 24,* 6609–6615.

Umdu, E. S., Tuncer, M., & Seker, E. (2009). Transesterification of *Nannochloropsis oculata* microalga's lipid to biodiesel on Al_2O_3 supported CaO and MgO catalysts. *Bioresource Technology, 100,* 2828–2831.

Vergini, S., Aravantinou, A. F., & Manariotis, I. D. (2016). Harvesting of freshwater and marine microalgae by common flocculants and magnetic microparticles. *Journal of Applied Phycology, 28,* 1041–1049.

Wahlen, B. D., Willis, R. M., & Seefeldt, L. C. (2011). Biodiesel production by simultaneous extraction and conversion of total lipids from microalgae, cyanobacteria, and wild mixed-cultures. *Bioresource Technology, 102,* 2724–2730.

Wang, L., Min, M., Li, Y., Chen, P., Chen, Y., Liu, Y., et al. (2010). Cultivation of green algae *Chlorella* sp. in different wastewaters from municipal wastewater treatment plant. *Applied Biochemistry and Biotechnology, 162,* 1174–1186.

Wen, Z., Yu, X., Tu, S. T., Yan, J., & Dahlquist, E. (2009). Intensification of biodiesel synthesis using zigzag micro-channel reactors. *Bioresource Technology, 100,* 3054–3060.

Xin, L., Hong-ying, H., Ke, G., & Ying-xue, S. (2010). Effects of different nitrogen and phosphorus concentrations on the growth, nutrient uptake, and lipid accumulation of a freshwater microalga *Scenedesmus* sp. *Bioresource Technology, 101,* 5494–5500.

Zhang, Y., Li, Y., Zhang, X., & Tan, T. (2015). Biodiesel production by direct transesterification of microalgal biomass with co-solvent. *Bioresource Technology, 196,* 712–715.

Zhang, X., Ma, Q., Cheng, B., Wang, J., Li, J., & Nie, F. (2012). Research on KOH/La-Ba-Al_2O_3 catalysts for biodiesel production via transesterification from microalgae oil. *Journal of Natural Gas Chemistry, 21,* 774–779.

Zheng, Y., Roberts, M., Kelly, J., Zhang, N., & Walker, T. (2015). Harvesting microalgae using the temperature-activated phase transition of thermoresponsive polymers. *Algal Research, 11,* 90–94.

Zheng, M., Skelton, R. L., & Mackley, M. R. (2007). Biodiesel reaction screening using oscillatory flow meso reactors. *Process Safety and Environment Protection, 85,* 365–371.

Zheng, H., Yin, J., Gao, Z., Huang, H., Ji, X., & Dou, C. (2011). Disruption of *Chlorella vulgaris* cells for the release of biodiesel-producing lipids: A comparison of grinding, ultrasonication, bead milling, enzymatic lysis, and microwaves. *Applied Biochemistry and Biotechnology, 164,* 1215–1224.

Zhou, N., Zhang, Y., Wu, X., Gong, X., & Wang, Q. (2011). Hydrolysis of Chlorella biomass for fermentable sugars in the presence of HCl and $MgCl_2$. *Bioresource Technology, 102,* 10158–10161.